

Table 2. Selected geometric parameters (Å, °) for (III)

Fe1—O3	2.030 (3)	Fe2—C13	1.812 (4)
Fe1—C1	2.042 (4)	Fe2—C14	1.745 (4)
Fe1—C2	2.071 (3)	O1—C5	1.237 (5)
Fe1—C9	1.832 (4)	O3—C7	1.246 (5)
Fe1—C10	1.817 (5)	C1—C2	1.431 (5)
Fe1—C11	1.760 (5)	C2—C3	1.502 (4)
Fe2—O1	2.036 (3)	C2—C5	1.447 (5)
Fe2—C3	2.067 (4)	C3—C4	1.429 (5)
Fe2—C4	2.034 (4)	C3—C7	1.446 (5)
Fe2—C12	1.815 (5)		
O3—Fe1—C1	88.6 (2)	C9—Fe1—C11	90.4 (2)
O3—Fe1—C2	80.7 (1)	C10—Fe1—C11	90.6 (2)
O3—Fe1—C9	91.0 (2)	O1—Fe2—C14	175.1 (2)
O3—Fe1—C10	90.3 (2)	Fe2—O1—C5	114.8 (2)
O3—Fe1—C11	178.1 (2)	Fe1—O3—C7	114.7 (3)
C9—Fe1—C10	105.4 (2)		
C1—C2—C5—O1	168.6 (5)	C4—C3—C7—O3	170.6 (6)
C1—C2—C3—C4	-103.9 (4)		

For both compounds, data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *maxUs* (Mackay *et al.*, 1999); program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997b); molecular graphics: *maxUs*; software used to prepare material for publication: *maxUs*.

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(Carbonato-*O,O'*)bis(propane-1,3-diyl-diamine-*N,N'*)cobalt(III) chloride monohydrate

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Abstract

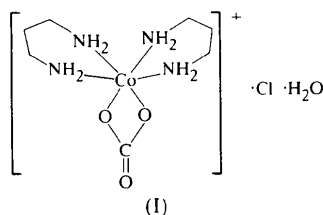
In the cation of the title compound, [Co(C₃H₁₀N₂)₂-(CO₃)Cl·H₂O] or [Co(pren)₂(CO₃)Cl·H₂O], where pren is trimethylenediamine (C₃H₁₀N₂), the metal atom is chelated by two pren ligands and a carbonate anion in a distorted octahedral geometry, with Co—N bond lengths in the range 1.922 (3)–1.945 (3) Å and Co—O bond lengths of 1.885 (3) and 1.901 (3) Å.

Comment

The fixation of atmospheric CO₂ by metal complexes is of special interest in environmental protection, because the fundamental understanding and application of the reaction may lead to some practical means to reduce the level of CO₂ present in the air. The development of an effective chemical method for CO₂ fixation is the

focus of numerous investigations (Behr, 1988). A variety of insertion reactions of CO₂ into metal complexes, particularly those of platinum(II) and cobalt(II), have been reported (Bernal *et al.*, 1993; Masuda *et al.*, 1994; Kitajima *et al.*, 1993; Baxter *et al.*, 1995; Egan *et al.*, 1995; Tsuboyama *et al.*, 1996). In preparing a cobalt(II) chloride complex with trimethylenediamine (pren), we found that the resulting solution is auto-oxidized in air and then readily reacts with atmospheric CO₂ to give the carbonate product.

The title compound, (I), consists of a [Co(pren)₂(CO₃)]⁺ cation, a Cl⁻ anion and a lattice water molecule. The cobalt(III) ion has distorted octahedral geom-



etry, being coordinated by four N atoms from two chelate diamine ligands and two O atoms from the carbonate anion. The most distorted bond angle in the octahedron is O2—Co1—O1 [68.18(12)°], as a result of chelation by the carbonate group. The Co—N bond lengths are in the range 1.922(3)–1.945(3) Å, similar to those of other cobalt(III) carbonates (Egan *et al.*, 1995; Tsuboyama *et al.*, 1996). The average Co—O bond distance (1.893 Å) is much shorter than the Co—O_{aqua} bonds found in [Co(en)₂(H₂O)₂]³⁺ (en is ethylenediamine; 1.94 Å; Ardon & Bino, 1985), suggesting that a carbonate ion binds more strongly than a water molecule. It is noteworthy that the Co—O distances in (I) are significantly shorter than those in [Co(pren)₂(CO₃)](ClO₄) (Co—O1 1.919 and Co—O2 1.953 Å; Bernal *et al.*, 1993), which may possibly be attributed to the much more extensive hydrogen bonding in (I).

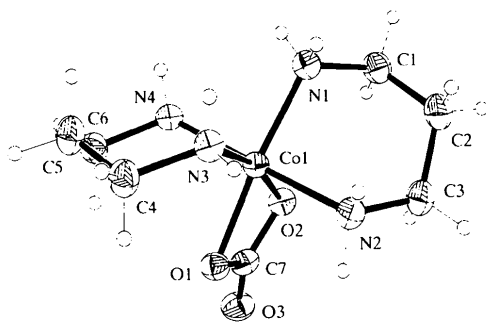


Fig. 1. ORTEP plot (Johnson, 1965) of the [Co(pren)₂(CO₃)]⁺ cation in (I). Displacement ellipsoids are shown at the 35% probability level and H atoms are drawn as small spheres of arbitrary radii.

Extensive hydrogen bonding plays a vital role in stabilizing the crystal structure of (I). The lattice water molecule and the two amine N atoms are donors in two hydrogen bonds to carbonate O atoms or to Cl⁻ ions; each of the carbonate O atoms forms one or two hydrogen bonds, and the Cl⁻ ion forms six hydrogen bonds (see Table 2). These hydrogen bonds extend the structure into two-dimensional layers parallel to the (10 $\bar{1}$) plane.

Experimental

The title compound was prepared by stirring a mixture of trimethylenediamine (1 mmol, 74 mg) and CoCl₂·6H₂O (1 mmol, 238 mg) in water (10 ml) for 24 h. The solution was allowed to stand at room temperature. After a few days dark-red crystals of (I) formed. Analysis found: C 26.0, H 6.8, N 17.4%; calculated for C₇H₂₂ClCoN₄O₄: C 26.2, H 6.9, N 17.5%.

Crystal data

[Co(C₃H₁₀N₂)₂(CO₃)]Cl·H₂O
M_r = 320.66
 Monoclinic
*P*2₁/*n*
a = 9.009 (2) Å
b = 6.756 (2) Å
c = 21.276 (9) Å
 β = 91.76 (1)°
V = 1294.3 (7) Å³
Z = 4
D_x = 1.646 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 6.5–15.0°
 μ = 1.542 mm⁻¹
T = 293 (2) K
 Prism
 0.45 × 0.40 × 0.35 mm
 Dark red

Data collection

Siemens R3m diffractometer
 ω scan
 Absorption correction:
 semi-empirical *via* ψ scan
 (Kopfmán & Huber, 1968)
T_{min} = 0.476, *T_{max}* = 0.608
 2428 measured reflections
 2275 independent reflections
 1817 reflections with
I > 2σ(*I*)

R_{int} = 0.021
 θ_{\max} = 25°
h = 0 → 10
k = 0 → 8
l = -25 → 25
 2 standard reflections
 every 150 reflections
 intensity decay: <2%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.043
wR (*F*²) = 0.115
S = 1.045
 2275 reflections
 155 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 0.4324P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.532 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.306 \text{ e \AA}^{-3}$
 Extinction correction:
 SHELXL97 (Sheldrick, 1997)
 Extinction coefficient:
 0.0047 (10)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Co1—O2	1.885 (3)	Co1—N2	1.945 (3)
Co1—O1	1.901 (3)	O1—C7	1.293 (5)
Co1—N3	1.922 (3)	O2—C7	1.294 (5)
Co1—N1	1.930 (3)	O3—C7	1.224 (5)
Co1—N4	1.937 (3)		
O2—Co1—O1	68.18 (12)	O1—Co1—N2	90.60 (13)
O2—Co1—N3	166.06 (12)	N3—Co1—N2	91.07 (14)
O1—Co1—N3	97.91 (13)	N1—Co1—N2	89.49 (14)
O2—Co1—N1	98.65 (13)	N4—Co1—N2	178.18 (13)
O1—Co1—N1	166.83 (12)	C1—N1—Co1	115.6 (3)
N3—Co1—N1	95.25 (14)	C3—N2—Co1	117.4 (2)
O2—Co1—N4	90.12 (13)	C4—N3—Co1	115.9 (3)
O1—Co1—N4	91.11 (13)	C6—N4—Co1	117.0 (2)
N3—Co1—N4	89.31 (13)	C7—O1—Co1	90.4 (2)
N1—Co1—N4	88.70 (13)	C7—O2—Co1	91.1 (2)
O2—Co1—N2	89.94 (13)		

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...Cl1 ⁱ	0.90	2.33	3.215 (4)	168
N1—H1B...O3 ⁱⁱ	0.88	2.38	2.982 (5)	126
N2—H2A...Cl1 ⁱⁱⁱ	0.95	2.49	3.317 (4)	146
N2—H2B...Cl1	0.93	2.95	3.459 (3)	116
N3—H3A...Cl1 ⁱ	0.81	2.72	3.226 (4)	123
N3—H3B...Cl1	0.83	2.44	3.202 (4)	154
N4—H4A...O3 ⁱⁱ	0.88	2.04	2.894 (4)	164
N4—H4B...O2 ^{iv}	0.91	2.00	2.865 (4)	159
O1W—H1WB...Cl1	1.00	2.28	3.263 (5)	168
O1W—H1WA...O1	0.98	1.88	2.867 (5)	180

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $x, 1+y, z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $1-x, -y, -z$.

The H atoms of the water molecule and of the amine groups were located from a difference map but not refined. The H atoms of the methylene groups were placed at calculated positions and allowed to ride on their respective parent atoms. All H atoms were assigned fixed isotropic displacement parameters.

Data collection: *SHELXTL-Plus* (Sheldrick, 1990a). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXS90* (Sheldrick, 1990b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP* (Johnson, 1965) in *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1264). Services for accessing these data are described at the back of the journal.

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catena-Poly[[bis(imidazole-*N*³)cadmium(II)]-bis(μ -thiocyanato)-*S*:*N*; *N*:*S*]

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Abstract

The title polymeric complex, [Cd(SCN)₂(C₃H₄N₂)₂]_n, exhibits an infinite chain structure in which each pair of Cd atoms is bridged by two η -1,3-SCN[−] groups. The unique Cd atom lies on an inversion centre and the coordination sphere is completed by two imidazole N atoms to form a CdS₂N₄ octahedron. The polymeric chains are further extended into two-dimensional sheets via N—H...S hydrogen bonds between the uncoordinated imidazole N atoms and the SCN[−] groups.

Comment

The structures of a few polymeric Lewis-base adducts of cadmium(II) thiocyanate, [Cd(SCN)₂(L)₂] (where L is 2-, 3- or 4-methylpyridine, benzylamine, dibenzylamine, tri-*m*-tolylphosphine or 1*H*-1,2,4-triazole), have been reported (Ram *et al.*, 1981; Taniguchi & Ouchi, 1987; Taniguchi *et al.*, 1987). In these compounds, the Lewis base (L) is a monofunctional ligand, which gives a one-dimensional structure with thiocyanate as a bridging ligand. We report here a similar Lewis-base adduct of Cd(SCN)₂, [Cd(SCN)₂(ImH)₂]_n, (I), in which imidazole (ImH) is a bifunctional ligand capable of both coordinating with a metal ion and donating a hydrogen bond (Andrew *et al.*, 1994a,b; Chow *et al.*,